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TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER
PW/3-22076/A/PCT

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)
10/070525

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/EP 00/08621	**September 4, 2000**	**September 10, 1999**

TITLE OF INVENTION
Trazinylaminostilbene derivative as fluorescent whitening agents

APPLICANT(S) FOR DO/EO/US
Georges Metzger, Serge Hauger, Fabienne Cuesta, Christophe Bulliard, Peter Rohringer and Marc Roger Grienenberger

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☑ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This express request to begin national examination procedures (35 U.S.C. 371(f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39 (1).
4. ☑ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☑ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☑ has been transmitted by the International Bureau. **(See attached Form PCT/IB/308)**
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ A translation of the International Application into English 35.U.S.C. 371(c)(2)).
7. ☑ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C.371(c)(3)).
   a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ have been transmitted by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☑ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☑ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included.

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.

12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.

13. ☑ **A FIRST preliminary amendment.**
    ☐ A SECOND or SUBSEQUENT preliminary amendment.

14. ☐ A substitute specification.

15. ☐ A change of power of attorney and/or address letter.

16. ☑ Other items or information: **(See attached Form PCT/ISA/210)**

U.S. APPLICATION NO. (if known, see 37 CFR 1.5)	INTERNATIONAL APPLICATION NO.	ATTORNEY'S DOCKET NUMBER
10/070525	PCT/EP 00/08621	PW/3-22076/A/PCT

17. ☑ The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492(a) (1)-(5)):

		CALCULATIONS PTO USE ONLY
Search Report has been prepared by the EPO or JPO	$890.00	
International preliminary examination fee paid to USPTO (37 CFR 1.482)	$710.00	
No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2))	$740.00	
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO	$1040.00	
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4)	$100.00	
ENTER APPROPRIATE BASIC FEE AMOUNT =		**$890.00**
Surcharge of **$130.00** for furnishing the oath of declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(e)).		$

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	**34** - 20 =	**14**	X **$18.00**	**$252.00**
Independent claims	**1** -3 =	**0**	X **$84.00**	$
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ **$280.00**	$
TOTAL OF ABOVE CALCULATIONS =				**$1,142.00**
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28).				$
SUBTOTAL =				**$1,142.00**
Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(f)). +				$
TOTAL NATIONAL FEE =				**$1,142.00**
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00** per property +				$
TOTAL FEES ENCLOSED =				$
			Amount to be: refunded	$
			charged	**$1,142.00**

a. ☐ A check in the amount of $_____ to cover the above fees is enclosed.

b. ☑ Please charge my Deposit Account No. 03-1935 in the amount of **$1,142.00** to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☑ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 03-1935. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

PLEASE ASSOCIATE THE ATTACHED APPLICATION WITH **CUSTOMER NUMBER 000324** AND SEND ALL CORRESPONDENCE TO:

JoAnn Villamizar, Ciba Specialty Chemicals Corporation
Patent Department
540 White Plains Road
P.O. Box 2005
Tarrytown, NY 10591-9005
DATE: MAR 06 2002

Kevin T. Mansfield
SIGNATURE

Kevin T. Mansfield
NAME
Reg. No. 31,635

CASE PW/3-22076/A/PCT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE PCT NATIONAL STAGE APPLICATION OF
GEORGES METZGER ET AL
INTERNATIONAL APPLICATION NO. PCT/EP 00/08621
FILED: SEPTEMBER 4, 2000
FOR: TRAZINYLAMINOSTILBENE DERIVATIVE
AS FLUORESCENT WHITENING AGENTS
U.S. APPLICATION NO: UNASSIGNED
35 USC 371 DATE:

Group Art Unit: unassigned
Examiner: unassigned

Assistant Commissioner for Patents
Washington, D.C. 20231

PRELIMINARY AMENDMENT

Sir:

Kindly amend this application as follows prior to calculation of the filing fee and consideration on the merits.

IN THE CLAIMS

Please cancel claims 26-30.

Kindly replace claims 6-7,10-12, 14-17, 19, 21-22, 24-25 and 32 by the following claims.

6. **(amended)** A compound according to claim 1 in which the amino acid from which each amino acid residue R_1 is derived is aspartic acid or iminodiacetic acid.

7. **(amended)** A compound according to claim 1 in which R_1 is a linear C_1-C_4-alkylene residue which is unsubstituted or substituted by hydroxy, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-hydroxy- or alkoxy-alkoxy, -OCOM, -$OCOC_1$-C_4-alkyl and M is as defined in claim 1.

10. **(amended)** A compound according to claim 1 in which the group R_2 represents a linear C_1-C_4-alkylene residue which is unsubstituted or substituted by hydroxy, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-hydroxy or alkoxyalkoxy, -OCOM, -$OCOC_1$-C_4-alkyl, -CO_2M, -CO_2C_1-C_4-alkyl, SO_3M, phenoxy which is unsubstituted or substituted by halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy, -CO_2M or -CO_2C_1-C_4-alkyl, NH_2 or mono- or disubstituted amino and M is as defined in claim 1.

11. **(amended)** A compound according to claim 10 in which the group R_2 represents a methylene, ethylene or propylene residue which is substituted by hydroxy, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-hydroxy- or alkoxy-alkoxy, -OCOM, -$OCOC_1$-C_4-alkyl, -CO_2M, -CO_2C_1-C_4-alkyl, SO_3M or di-C_1-C_4-alkylamino.

12. **(amended)** A compound according to claim 10 in which R_2 is hydoxyethyl, hydroxypropyl, ethoxyethyl, hydroxyethoxyethyl, methoxyethoxyethyl, an acetic or propionic acid residue or methyl or ethyl esters thereof, an ethyl or methyl acetate, dimethylaminoethyl or ethyl sulphonic acid or the sodium salt thereof.

14. **(amended)** A compound according to claim 1 in which each R_2 is phenyl which is unsubstituted or substituted by 1 to 3 SO_3M, SO_2NHC_1-C_4-alkyl,-SO_2NH_2, -CO_2M, -CO_2C_1-C_4-alkyl, -$CONH_2$, -$CONHC_1$-C_4-alkyl, -$NHCOC_1$-C_4-alkyl or mono- or disubstituted amino groups, wherein M is as defined in claim 1.

15. **(amended)** A compound according to claim 14 in which each R_2 is phenyl which is unsubstituted or substituted by one SO_3M, -SO_2NH_2 or -$NHCOC_1$-C_4-alkyl group.

16. **(amended)** A compound according to claim 14 in which each R_2 is phenyl.

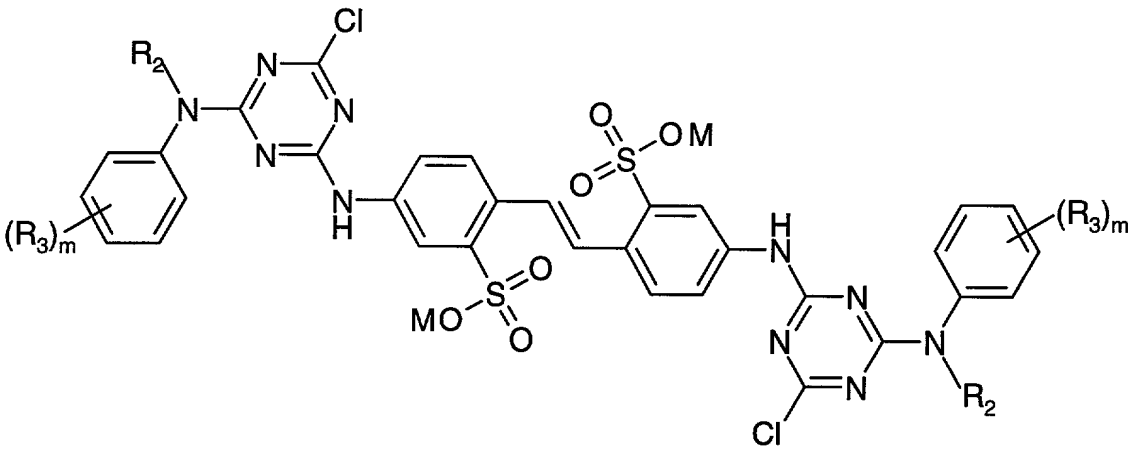
17 **(amended)** A compound according to claim 1 in which R_3 represents hydrogen, C_1-C_4-alkyl, halogen, cyano, SO_3M, -SO_2NH_2, SO_2NHC_1-C_4-alkyl, -CO_2M, -CO_2C_1-C_4-alkyl, -$CONH_2$, -$CONHC_1$-C_4-alkyl, or -$NHCOC_1$-C_4-alkyl, M being defined as in claim 1 and m is 1.

19. **(amended)** A compound according to claim 1 in which M is hydrogen, Na, K, Ca, Mg, ammonium, mono-, di-, tri- or tetra-C_1-C_4alkylammonium, mono-, di- or tri-C_1-C_4-hydroxyalkylammonium or ammonium that is di- or tri-substituted with a mixture of C_1-C_4-alkyl and C_1-C_4-hydroxyalkyl groups.

21. **(amended)** A compound of formula 1 according to claim 1 in which:
R_1 is an amino acid residue derived from aspartic acid or iminodiacetic acid,
R_2 is hydroxyethyl,
R_3 is hydrogen and
M is sodium.

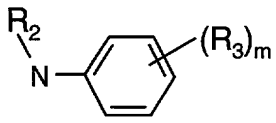
22. **(amended)** A compound of formula 1 according to claim 1 in which:
R_1 is a 2-methoxyethylamino residue,
R_2 is a sodium acetate residue,
R_3 is hydrogen and
M is sodium.

24. **(amended)** A process for the preparation of a compound of the formula (1) according to claim 1, which comprises reacting the compound of formula



(5)

with a compound capable of introducing a group R_1 in place of X, in which R_1 R_2, R_3, M and m are as defined in claim 1.

25. **(amended)** A process for the preparation of a compound of formula (1) according to claim 1 by reacting, under known reaction conditions, cyanuric chloride, successively, in any desired sequence, with each of 4,4'-diamino-2,2'-stilbene disulphonic acid, an amino compound capable of introducing a group  in which R_2, R_3 and m have their previous significance, and a

compound capable of introducing a group R_1, in which R_1 is as defined in claim 1.

32. **(amended)** A composition according to claim 31 containing water and, in each case based on the weight of the formulation, from 3 to 25% by weight of the fluorescent whitening agent and also 0 to 60% of auxiliaries.

Please add the following claims.

-- 33. **(new)** A method for the fluorescent whitening of a substrate comprising contacting the substrate with a compound having the formula (1) as defined in claim 1.

34. **(new)** A method according to claim 33, wherein the substrate is paper and the compound of formula (1) is applied to the paper substrate in the form of a paper coating composition, or directly in the size press.

35. **(new)** A method according to claim 34 for the fluorescent whitening of a paper surface, comprising contacting the paper surface with a coating composition comprising a white pigment; a binder dispersion; optionally a water-soluble co-binder; and a sufficient amount of a fluorescent whitening agent having the formula (1), to ensure that the treated paper contains 0.01 to 1 % by weight, based on the white pigment, of the fluorescent whitening agent of the formula (1).

36. **(new)** A method according to claim 34 for the fluorescent whitening of a paper surface comprising contacting the paper in the size press with an aqueous solution containing a size, optionally an inorganic or organic pigment and 0.1 to 20g/l of a fluorescent whitening agent of the formula (1).

37. **(new)** A method according to claim 33, wherein the substrate is a textile material.

38. **(new)** A method according to claim 37, wherein the textile material is washed with a household or industrial washing agent comprising an effective amount of a fluorescent whitening agent of the formula (1).

39. **(new)** A method for the prevention of a colour dye stain caused in the course of processing a silver halide photographic light-sensitive material by a colour developer and a bleach-fix bath, comprising incorporating a compound having the formula (1) as defined in claim 1 into the colour developer and/or the bleach-fix bath.--

REMARKS

Claims 1-25 and 31-39 are pending. Claims 6-7,10-12, 14-17, 19, 21-22, 24-26 and 32 have been amended by replacement. Said claims have been amended to reduce filing fees by reducing the number of independent claims and eliminating multiple dependency, and to provide minor clarification by eliminating multiple ranges. No other claims have been amended. Claims 33-39 have been added.

Another version of the amended claims, showing the changes relative to the previous version, is appended. Additions are shown by underlining. Deletions are shown by strikethrough rather than bracketing since the claims may contain bracketing that is to remain.

Newly added claims 33-39 are supported by originally filed claims 26-30 and the disclosure from page 9, last paragraph through page 15, third paragraph. No new matter has been added.

Applicants aver that the claims are now in proper form for examination. An Action on the merits of the claims is respectfully awaited.

Respectfully submitted,

Kevin T. Mansfield

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Agent for Applicants
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Marked-up Version of Amended Claims

6. **(amended)** A compound according to ~~any of~~ claims 1 ~~to 5~~ in which the amino acid from which each amino acid residue R_1 is derived is aspartic acid or iminodiacetic acid.

7. **(amended)** A compound according to claims 1 ~~or 2~~ in which R_1 is a linear C_1-C_4-alkylene residue which is unsubstituted or substituted by hydroxy, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-hydroxy- or alkoxy-alkoxy, -OCOM, -OCOC_1-C_4-alkyl~~,~~ and M ~~being~~ is as ~~previously~~ defined in claim 1.

10. **(amended)** A compound according to ~~any one of~~ claims 1 ~~to 9~~ in which the group R_2 represents a linear C_1-C_4-alkylene residue which is unsubstituted or substituted by hydroxy, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-hydroxy or alkoxyalkoxy, -OCOM, -OCOC_1-C_4-alkyl, -CO_2M, -CO_2C_1-C_4-alkyl, SO_3M, phenoxy which is unsubstituted or substituted by halogen, C_1-C_4-alkyl, C_1 -C_4-alkoxy, -CO_2M or -CO_2C_1-C_4-alkyl, NH_2 or mono- or disubstituted amino and M is as defined in claim 1.

11. **(amended)** A compound according to claim 10 in which the group R_2 represents a methylene, ethylene or propylene residue which is substituted by hydroxy, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-hydroxy- or alkoxy-alkoxy, -OCOM, -OCOC_1-C_4-alkyl, -CO_2M, -CO_2C_1-C_4-alkyl, SO_3M or di-C_1-C_4-alkylamino~~, whereby M is as defined in claim 1~~.

12. **(amended)** A compound according to claims 10 ~~or 11~~ in which R_2 is hydoxyethyl, hydroxypropyl, ethoxyethyl, hydroxyethoxyethyl, methoxyethoxyethyl, an acetic or propionic acid residue or methyl or ethyl esters thereof, an ethyl or methyl acetate, dimethylaminoethyl or ethyl sulphonic acid or the sodium salt thereof.

14. **(amended)** A compound according to claims 1 ~~or 2~~ in which each R_2 is phenyl which is unsubstituted or substituted by 1 to 3 SO_3M, SO_2NHC_1-C_4-alkyl,-SO_2NH_2, -CO_2M, -CO_2C_1-C_4-alkyl, -$CONH_2$, -CONHC$_1$-C_4-alkyl, -NHCOC$_1$-C_4-alkyl or mono- or disubstituted amino groups, wherein M is as defined in claim 1.

15. **(amended)** A compound according to claims 14 in which each R_2 is phenyl which is unsubstituted or substituted by one SO_3M, -SO_2NH_2 or -NHCOC$_1$-C_4-alkyl group.

16. **(amended)** A compound according to claims 14 ~~or 15~~ in which each R_2 is phenyl.

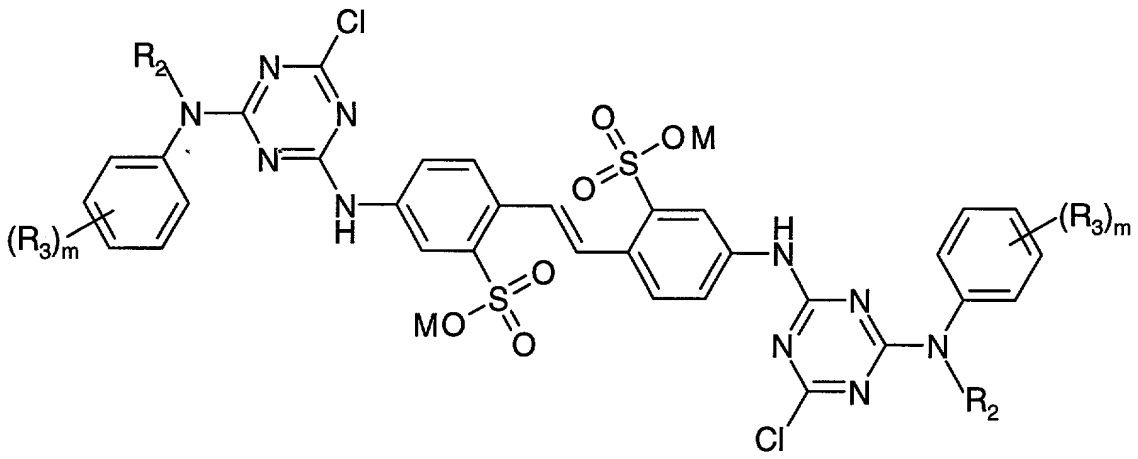
17 **(amended)** A compound according to ~~any one of the preceding~~ claims 1 in which R_3 represents hydrogen, C_1-C_4-alkyl, halogen, cyano, SO_3M, $-SO_2NH_2$, SO_2NHC_1-C_4-alkyl, $-CO_2M$, $-CO_2C_1$-C_4-alkyl, $-CONH_2$, $-CONHC_1$-C_4-alkyl, or $-NHCOC_1$-C_4-alkyl, M being defined as in claim 1 and m is 1.

19. **(amended)** A compound according to ~~any of the preceding~~ claims 1 in which M is hydrogen, Na, K, Ca, Mg, ammonium, mono-, di-, tri- or tetra-C_1-C_4alkylammonium, mono-, di- or tri-C_1-C_4-hydroxyalkylammonium or ammonium that is di- or tri-substituted with a mixture of C_1-C_4-alkyl and C_1-C_4-hydroxyalkyl groups.

21. **(amended)** A compound of formula 1 according to claim 1 in which:
R_1 is an amino acid residue derived from aspartic acid or iminodiacetic acid,
R_2 is hydroxyethyl,
R_3 is hydrogen and
M is sodium.

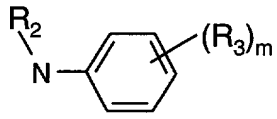
22. **(amended)** A compound of formula 1 according to claim 1 in which:
R_1 is a 2-methoxyethylamino residue,
R_2 is a sodium acetate residue,
R_3 is hydrogen and
M is sodium.

24. **(amended)** A process ~~Use of the compound of formula (5) of claim 23~~ for the preparation of a compound of the formula (1) according to claim 1, which comprises reacting the compound of formula



(5)

with a compound capable of introducing a group R_1 in place of X, in which R_1 R_2, R_3, M and m are as defined in claim 1.

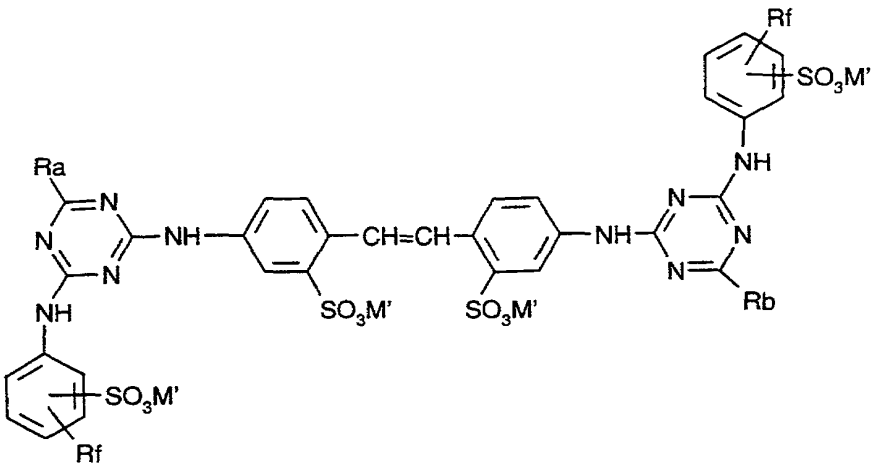
25. **(amended)** A process for the preparation of a compound of formula (1) according to claim 1 by reacting, under known reaction conditions, cyanuric chloride, successively, in any desired sequence, with each of 4,4'-diamino-2,2'-stilbene disulphonic acid, an amino compound capable of introducing a group  in which R_2, R_3 and m have their previous significance, and a compound capable of introducing a group R_1, in which R_1 is as defined in claim 1~~has its previous significance~~.

32. **(amended)** A~~Brightener~~ compositions according to claim 31 containing water and, in each case based on the weight of the formulation, from 3 to 25% by weight~~, preferably from 5 to 15% by weight~~ of the ~~above defined~~ fluorescent whitening agent ~~mixture~~ and also 0 to 60%~~, preferably 5 to 50% by weight,~~ of auxiliaries.

TRIAZINYLAMINOSTILBENE DERIVATIVE AS FLUORESCENT WHITENING AGENTS

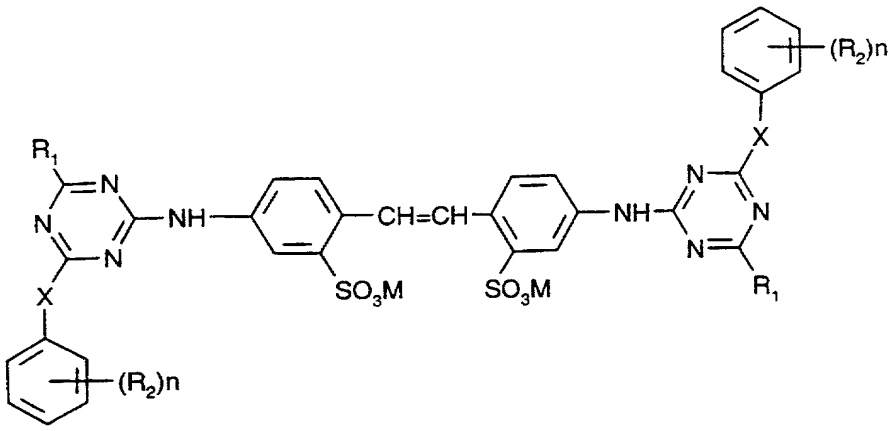
The present invention relates to new 4,4'-diaminostilbene-2,2'-disulfonic acid compounds which are useful as fluorescent whitening agents or for removing stain in photographic materials.

In WO 96/00221, there are described optical brightening agents for textiles, paper etc. The disclosed compounds have the formula:



in which R_a and R_b are the same or different and each has the formula $-NR_cR_d$ in which R_c is hydrogen; C_1-C_6alkyl which is optionally substituted by at least one of mercapto, C_1-C_6thioalkyl, OH and SO_3M' in which M' is hydrogen, a colourless cation or an amine-derived cation; or $-R_e(CO_2M')_x$ in which R_e is an aliphatic moiety having 1-6 carbon atoms, those valencies not bonded with groups CO_2M' being bonded with at least one of hydrogen, mercapto, C_1-C_6thioalkyl, OH and SO_3M' in which M' has its previous significance and x is an integer from 1 to 4, provided that, when R_c is C_1-C_6alkyl which is optionally substituted by at least one of mercapto, C_1-C_6thioalkyl, OH and SO_3M', R_c is substituted with at least both of OH and SO_3M'; R_d is R_c, hydrogen or C_3-C_6alkyl, provided that R_c and R_d cannot both be hydrogen and that, when one of R_c and R_d is hydrogen, the other cannot be $-(NHCH_2CO_2H)$; or R_c and R_d, together with the nitrogen atom, form a ring having from 5-6 members only, one of which is heterocyclic, which ring is singly substituted with -COOM' or $-SO_3M'$; and each R_f, independently, is hydrogen, methyl, C_1-C_6alkoxy or halogen.

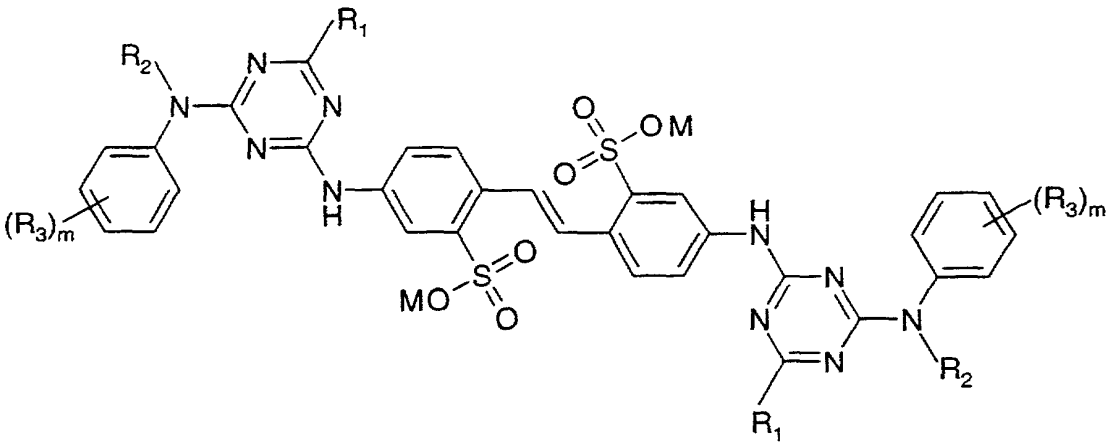
Furthermore, WO 98/42685 describes similar compounds having the formula:



in which X is O or, preferably, NH; M is hydrogen, an alkali metal atom, ammonium or a cation formed from an amine; each R_1, independently, is an amino acid residue from which a hydrogen atom on the amino group has been removed; n is 1 or 2; and each R_2, independently, is hydrogen, C_1-C_3alkyl, halogen, cyano, COOR in which R is hydrogen or C_1-C_3alkyl, CONH-R in which R has its previous significance, SO_2NH-R in which R has its previous significance, NH-COR in which R has its previous significance, SO_3M in which M has its previous significance or, when n is 1, R_2 can also be CO-R_3 in which R_3 is C_1-C_3alkyl or phenyl, certain compounds being excluded, and their use as fluorescent whitening agents.

A new class of 4,4'-diaminostilbene-2,2'-disulfonic acid compounds has now been found most of which are useful as fluorescent whitening agents and which have superior properties to, and are more readily prepared than the compounds disclosed in WO 96/00221 and in WO 98/42685. Furthermore, the new compounds are useful for removing stain in photographic materials.

Accordingly, the present invention provides new compounds having the formula:



(1)

wherein each

R_1 represents, independently, a linear C_1-C_4-alkylene residue which is unsubstituted or substituted by hydroxy, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-hydroxy- or alkoxy-alkoxy, -OCOM, -$OCOC_1$-C_4-alkyl, or an amino acid residue from which a hydrogen atom on the amino group has been removed; each

R_2 represents, independently, a linear C_1-C_4-alkylene residue which is unsubstituted or substituted by hydroxy, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-hydroxy- or alkoxy-alkoxy, -OCOM, -$OCOC_1$-C_4-alkyl, -CO_2M, CO_2C_1-C_4-alkyl SO_3M or phenoxy which is unsubstituted or substituted by halogen, C_1-C_4-alkyl or C_1 -C_4-alkoxy, -CO_2M or -CO_2C_1-C_4-alkyl, NH_2 or mono- or disubstituted amino; or phenyl which is unsubstituted or substituted by 1 to 3 SO_3M, SO_2NHC_1-C_4- alkyl,-SO_2NH_2, -CO_2M, -CO_2C_1-C_4-alkyl, -$CONH_2$, -$CONHC_1$-C_4-alkyl, -$NHCOC_1$-C_4-alkyl or mono- or disubstituted amino groups; each

R_3 represents, independently, hydrogen, C_1-C_4-alkyl, halogen, cyano, SO_3M, -SO_2NH_2, SO_2NHC_1-C_4-alkyl, -CO_2M, -CO_2C_1-C_4-alkyl, -$CONH_2$, -$CONHC_1$-C_4-alkyl, or -$NHCOC_1$-C_4-alkyl;

M is hydrogen, an alkali metal atom, ammonium or a cation formed from an amine and

m is an integer of 1 to 3.

Within the scope of the compounds of formula (1) both of the R_1 groups, the R_2 groups and the R_3 groups are preferably identical.

Further preferred compounds of formula (1) are those in which each of the amino acid residues R_1 is the same and each has the formula -NH-CH(CO_2H)-R_4 in which R_4 is

hydrogen or a group having the formula $-CHR_5R_6$ in which R_5 and R_6, independently, are hydrogen or C_1-C_4-alkyl optionally substituted by one or two substituents selected from hydroxy, thio, methylthio, amino, carboxy, sulfo, phenyl, 4-hydroxyphenyl, 3,5-diiodo-4-hydroxyphenyl, β-indolyl, β-imidazolyl and $NH=C(NH_2)NH-$.

Particularly useful compounds of formula (1) are those in which the amino acid from which the amino acid residues R_1 are derived is glycine, alanine, sarcosine, serine, cysteine, phenylalanine, tyrosine (4-hydroxyphenylalanine), diiodotyrosine, tryptophan (β-indolylalanine), histidine ((β-imidazolylalanine), α-aminobutyric acid, methionine, valine (α-aminoisovaleric acid), norvaline, leucine (α-aminoisocaproic acid), isoleucine (α-amino-β-methylvaleric acid), norleucine (α-amino-n-caproic acid), arginine, ornithine (α,δ-diaminovaleric acid), lysine (α,ε-diaminocaproic acid), aspartic acid (aminosuccinic acid), glutamic acid (α-aminoglutaric acid), threonine, hydroxyglutamic acid or taurine, or a mixture or an optical isomer thereof.

Especially preferred compounds are those in which the amino acid from which the amino acid residues R_1 are derived is sarcosine, taurine, glutamic acid or aspartic acid, aspartic acid or iminodiacetic acid being the most desirable.

Further preferred compounds of formula (1) are those in which R_1 is a linear C_1-C_4-alkylene residue which is unsubstituted or substituted by hydroxy, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-hydroxy- or alkoxy-alkoxy, -OCOM, $-OCOC_1$-C_4-alkyl, especially those in which R_1 is a linear C_1-C_4-alkylene residue which is unsubstituted or substituted by hydroxy, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-hydroxy- or alkoxy-alkoxy and, most preferably, those in which R_1 is a linear C_1-C_4-alkylene residue which is substituted by hydroxy or C_1-C_4-alkoxy, M being as previously defined.

With regard to the residue R_2, this is preferably a linear C_1-C_4-alkylene residue which is unsubstituted or substituted by hydroxy, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-hydroxy or alkoxyalkoxy, -OCOM, $-OCOC_1$-C_4-alkyl, $-CO_2M$, $-CO_2C_1$-C_4-alkyl, SO_3M, phenoxy which is unsubstituted or substituted by halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy, $-CO_2M$ or $-CO_2C_1$-C_4-alkyl, NH_2 or mono- or disubstituted amino, most preferably, a methylene, ethylene or propylene residue which is substituted by hydroxy, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-hydroxy-

or alkoxy-alkoxy, -OCOM, -$OCOC_1$-C_4-alkyl, -CO_2M, -CO_2C_1-C_4-alkyl, SO_3M or di-C_1-C_4-alkylamino.

Compounds of particular interest are those in which R_2 is hydoxyethyl, hydroxypropyl, ethoxyethyl, hydroxyethoxyethyl, methoxyethoxyethyl, an acetic or propionic acid residue or methyl or ethyl esters thereof, an ethyl or methyl acetate, dimethylaminoethyl or ethyl sulphonic acid or the sodium salt thereof, an hydoxyethyl or a sodium acetate residue being most preferred.

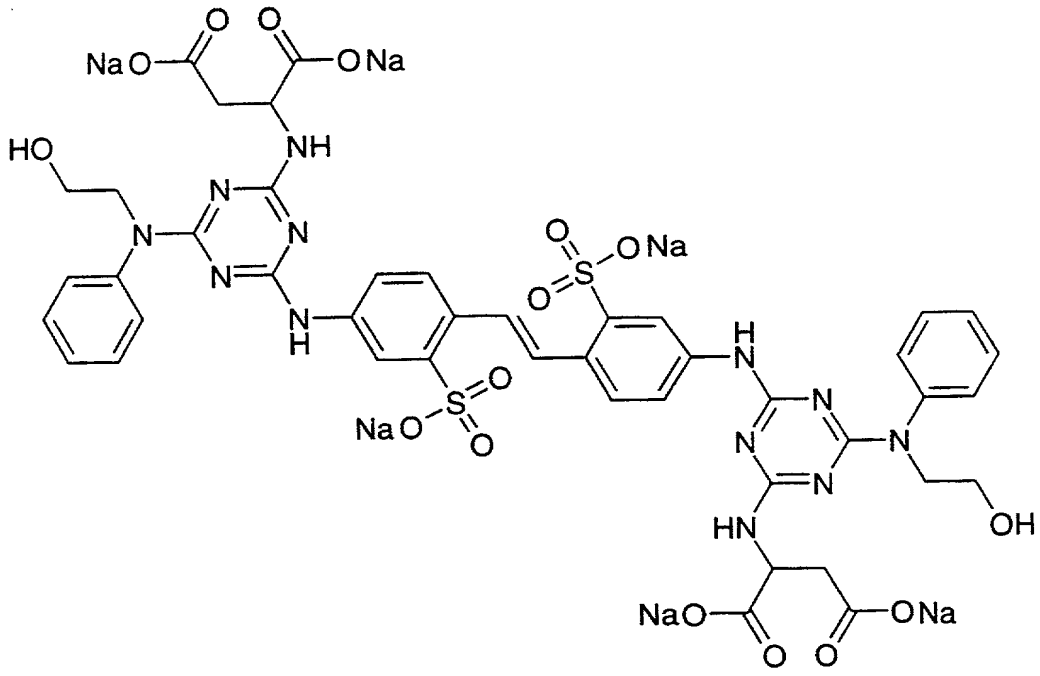
Further interesting compounds are those in which each R_2 is phenyl which is unsubstituted or substituted by 1 to 3 SO_3M, SO_2NHC_1-C_4- alkyl,-SO_2NH_2, -CO_2M, -CO_2C_1-C_4-alkyl, -$CONH_2$, -$CONHC_1$-C_4-alkyl, -$NHCOC_1$-C_4-alkyl or mono- or disubstituted amino groups

Of especial interest are compounds in which each R_2 is phenyl which is unsubstituted or substituted by one SO_3M,-SO_2NH_2 or -$NHCOC_1$-C_4-alkyl group, however, the phenyl group is preferably unsubstituted.

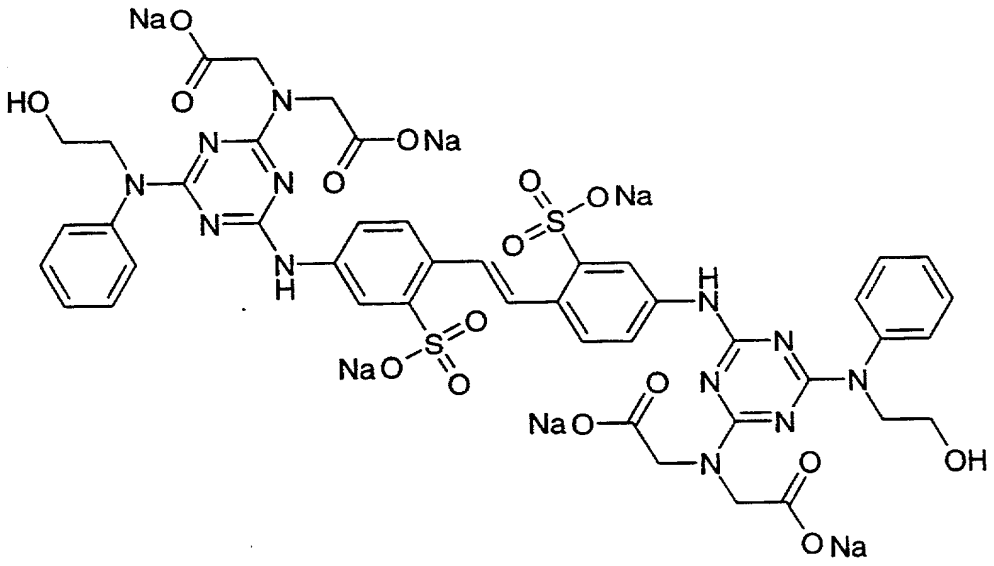
Further preferred compounds of formula (1) are those in which each R_3 residue represents hydrogen, C_1-C_4-alkyl, halogen, cyano, SO_3M, -SO_2NH_2, SO_2NHC_1-C_4-alkyl, -CO_2M, -CO_2C_1-C_4-alkyl, -$CONH_2$, -$CONHC_1$-C_4-alkyl, or -$NHCOC_1$-C_4-alkyl, those in which R_3 represents hydrogen being most preferred.

In the formulae of the above compounds, M is preferably hydrogen, Na, K, Ca, Mg, ammonium, mono-, di-, tri- or tetra-C_1-C_4alkylammonium, mono-, di- or tri-C_1-C_4-hydroxyalkylammonium or ammonium that is di- or tri-substituted with a mixture of C_1-C_4-alkyl and C_1-C_4-hydroxyalkyl groups, especially hydrogen or Na and m is preferably 1.

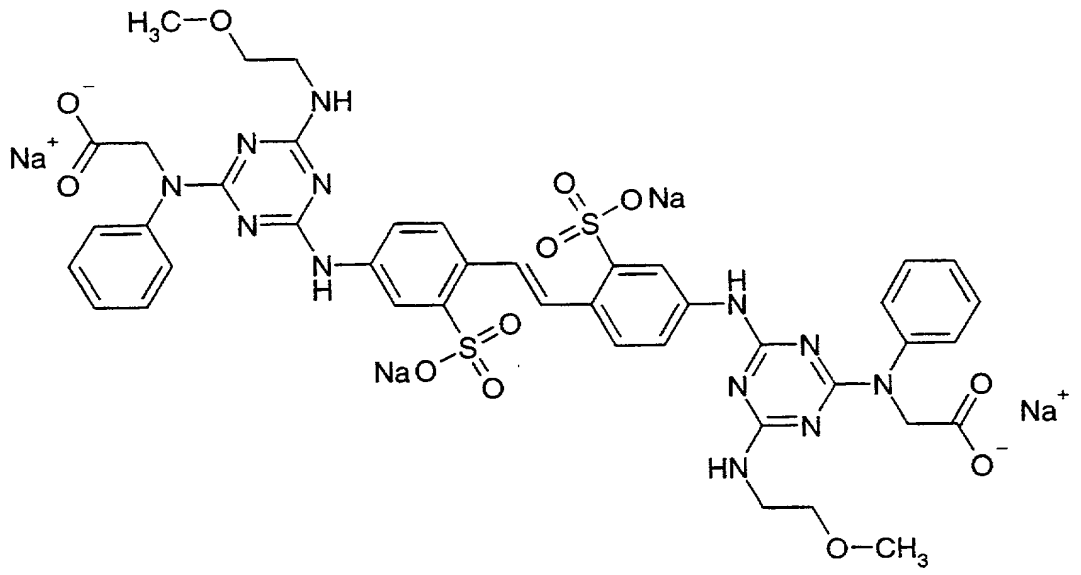
Compounds of most particular interest are those of the formula:



(2),

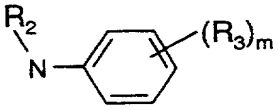


(3) and



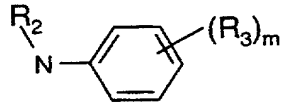
(4).

The compounds of formula (1) may be produced by reacting, under known reaction conditions, cyanuric chloride, successively, in any desired sequence, with each of 4,4'-diamino-2,2'-stilbene disulfonic acid, an amino compound capable of introducing a group

 in which R_2, R_3 and m have their previous significance, and a

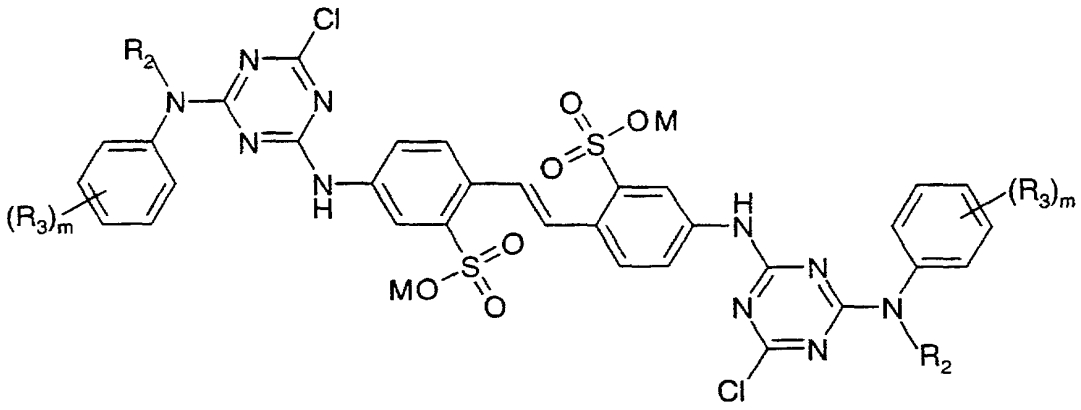
compound capable of introducing a group R_1, in which R_1 has its previous significance.

Preferably, 2 moles of cyanuric chloride are initially reacted with 1 mole of 4,4'-diamino-2,2'-stilbene disulfonic acid, then with an amino compound capable of introducing a group

 in which R_2, R_3 and m have their previous significance, and, finally, and

with a compound capable of introducing a group R_1, in which R_1 has its previous significance.

Consequently, a further aspect of the invention is a compound of formula:



(5)

in which R_2, R_3, M and m are as previously defined.

Within the scope of the compounds of formula (5) both of the two R_2 groups and the two R_3 groups are preferably identical.

With regard to the residue R_2, this is preferably a methylene, ethylene or propylene residue which is substituted by hydroxy, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-hydroxy- or alkoxy-alkoxy, -OCOM, -$OCOC_1$-C_4-alkyl, -CO_2M, -CO_2C_1-C_4-alkyl, SO_3M or di-C_1-C_4-alkylamino.

Compounds of particular interest are those in which R_2 is hydoxyethyl, hydroxypropyl, ethoxyethyl, hydroxyethoxyethyl, methoxyethoxyethyl, an acetic or propionic acid residue or methyl or ethyl esters thereof, an ethyl or methyl acetate, dimethylaminoethyl or ethyl sulphonic acid or the sodium salt thereof, hydoxyethyl or a sodium acetate residue being most preferred.

Further interesting compounds are those in which each R_2 is phenyl which is unsubstituted or substituted by 1 to 3 SO_3M, SO_2NHC_1-C_4- alkyl,-SO_2NH_2, -CO_2M, -CO_2C_1-C_4-alkyl, -$CONH_2$, -$CONHC_1$-C_4-alkyl, -$NHCOC_1$-C_4-alkyl or mono- or disubstituted amino groups

Of especial interest are compounds in which each R_2 is phenyl which is unsubstituted or substituted by one SO_3M,-SO_2NH_2 or -$NHCOC_1$-C_4-alkyl group, however, the phenyl group is preferably unsubstituted.

Further preferred compounds of formula (5) are those in which each R_3 residue represents hydrogen, C_1-C_4-alkyl, halogen, cyano, SO_3M, $-SO_2NH_2$, SO_2NHC_1-C_4-alkyl, $-CO_2M$, $-CO_2C_1$-C_4-alkyl, $-CONH_2$, $-CONHC_1$-C_4-alkyl, or $-NHCOC_1$-C_4-alkyl, those in which R_3 represents hydrogen being most preferred.

In the formulae of the above compounds, M is preferably hydrogen, Na, K, Ca, Mg, ammonium, mono-, di-, tri- or tetra-C_1-C_4alkylammonium, mono-, di- or tri-C_1-C_4-hydroxyalkylammonium or ammonium that is di- or tri-substituted with a mixture of C_1-C_4-alkyl and C_1-C_4-hydroxyalkyl groups, especially hydrogen or Na and m is preferably 1.

The starting materials are known compounds which are readily available.

A further aspect of the invention is a composition for whitening synthetic or natural organic materials or for removing stain from photographic materials, which contains water, a fluorescent whitening agent of formula (1) and, optionally, auxiliaries.

More specifically, such brightener compositions contain water and, in each case based on the weight of the formulation, from 3 to 25% by weight, preferably from 5 to 15% by weight of the above defined fluorescent whitening agent mixture and also 0 to 60%, preferably 5 to 50% by weight, of auxiliaries.

Suitable auxiliaries include, for example, anionic or non-ionic dispersants from the class of ethylene oxide adducts with fatty alcohols, higher fatty acids or alkyl phenols or ethylenediamine ethylene oxide-propylene oxide adducts, copolymers of N-vinylpyrrolidone with 3-vinylpropionic acid, water retention aids, such as ethylene glycol, glycerol or sorbitol, or biocides.

Most of the compounds of formula (1) are excellent fluorescent whitening agents for synthetic or natural substrates such as textiles and, in particular, for paper and also in detergent compositions.

Accordingly, the present invention further provides a method for the fluorescent whitening of a substrate comprising contacting the substrate with a compound having the formula (1).

When used for the fluorescent whitening of paper, the compound of formula (1) according to the present invention may be applied to the paper substrate in the form of a paper coating composition, or directly in the size press.

In one preferred aspect, the present invention provides a method for the fluorescent whitening of a paper surface, comprising contacting the paper surface with a coating composition comprising a white pigment; a binder dispersion; optionally a water-soluble co-binder; and sufficient of a fluorescent whitening agent having the formula (1) according to the present invention, to ensure that the treated paper contains 0.01 to 1 % by weight, based on the white pigment, of a fluorescent whitening agent having the formula (1).

As the white pigment component of the paper coating composition used according to the method of the present invention, there are preferred inorganic pigments, e.g., aluminium or magnesium silicates, such as China clay and kaolin and, further, barium sulfate, satin white, titanium dioxide , calcium carbonate (chalk) or talcum; as well as white organic pigments.

The paper coating compositions used according to the method of the present invention may contain, as binder, inter alia, plastics dispersions based on copolymers of butadiene/styrene, acrylonitrile/butadiene/styrene, acrylic acid esters, acrylic acid esters/styrene/acrylonitrile, ethylene/vinyl chloride and ethylene/vinyl acetate; or homopolymers, such as polyvinyl chloride, polyvinylidene chloride, polyethylene and polyvinyl acetate or polyurethanes. A preferred binder consists of styrene/butyl acrylate or styrene/butadiene/ acrylic acid copolymers or styrene/butadiene rubbers. Other polymer latices are described, for example, in U.S.Patent Specifications 3,265,654, 3,657,174, 3,547,899 and 3,240,740.

The optional water-soluble protective colloid may be, e.g., soya protein, casein, carboxymethylcellulose, natural or modified starch, chitosan or a derivative thereof or, especially, polyvinyl alcohol. The preferred polyvinyl alcohol protective colloid component may have a wide range of saponification levels and molecular weights; e.g. a saponification level ranging from 40 to 100; and an average molecular weight ranging from 10,000 to 100,000.

Recipes for coating compositions for paper are described, for example, in J.P. Casey "Pulp and Paper"; Chemistry and Chemical Technology, 2nd edition, Volume III, pages1684-1649 and in "Pulp and Paper Manufacture", 2nd and 5th edition, Volume II, page497 (McGraw-Hill).

The paper coating compositions used according to the method of the present invention preferably contain 10 to 70% by weight of a white pigment. The binder is preferably used in an amount which is sufficient to make the dry content of polymeric compound up to 1 to 30% by weight, preferably 5 to 25% by weight, of the white pigment. The amount of fluorescent brightener preparation used according to the invention is calculated so that the fluorescent brightener is preferably present in amounts of 0.01 to 1% by weight, more preferably 0.05 to 1% by weight, and especially 0.05 to 0.6% by weight, based on the white pigment.

The paper coating composition used in the method according to the invention can be prepared by mixing the components in any desired sequence at temperature from 10 to 100°C, preferably 20 to 80°C. The components here also include the customary auxiliaries which can be added to regulate the rheological properties, such as viscosity or water retention capacity, of the coating compositions. Such auxiliaries are, for example, natural binders, such as starch, casein, protein or gelatin, cellulose ethers, such as carboxyalkylcellulose or hydroxyalkylcellulose, alginic acid, alginates, polyethylene oxide or polyethylene oxide alkyl ethers, copolymers of ethylene oxide and propylene oxide, polyvinyl alcohol, water-soluble condensation products of formaldehyde with urea or melamine, polyphosphates or polyacrylic acid salts.

The coating composition used according to the method of the present invention is preferably used to produce coated printed or writing paper, or special papers such as cardboard or photographic papers.

The coating composition used according to the method of the invention can be applied to the substrate by any conventional process, for example with an air blade, a coating blade, a roller, a doctor blade or a rod, or in the size press, after

which the coatings are dried at paper surface temperatures in the range from 70 to 200°C, preferably 90 to 130°C, to a residual moisture content of 3-8%, for example with infra-red driers and/or hot-air driers. Comparably high degrees of whiteness are thus achieved even at low drying temperatures.

By the use of the method according to the invention, the coatings obtained are distinguished by optimum distribution of the dispersion fluorescent brightener over the entire surface and by an increase in the level of whiteness thereby achieved, by a high fastness to light and to elevated temperature (e.g. stability for 24 hours at 60-100°C.) and excellent bleed-fastness to water.

In a second preferred aspect, the present invention provides a method for the fluorescent whitening of a paper surface comprising contacting the paper in the size press with an aqueous solution containing a size, optionally an inorganic or organic pigment and 0.1 to 20g/l of a fluorescent whitening agent having the formula (1). Preferably, the size is starch, a starch derivative or a synthetic sizing agent, especially a water-soluble copolymer.

In a third preferred aspect, the brighteners defined above are of particular importance for the treatment of textile fabrics. The treatment of textile substrates is advantageously carried out in an aqueous medium in which the particular optical brighteners are present in a finely divided form (suspensions, so-called microdispersions and in some cases solutions). Dispersing agents, stabilisers, wetting agents and further auxiliaries can optionally be added during the treatment.

The treatment is usually carried out at temperatures of from about 20° to 140°C, for example at the boiling point of the bath, or in the region thereof (about 90°C). For the finishing, according to the invention, of textile substrates it is also possible to use solutions or emulsions in organic solvents, as are used in dyeing practice in so-called solvent dyeing (pad-thermofix method and the exhaustion dyeing process in dyeing machines).

The optical brighteners which can be used according to the present invention can also be employed, for example, in the following use forms:

(a) In mixtures with so-called "carriers", wetting agents, softeners, swelling agents, antioxidants, light stabilisers, heat stabilisers and chemical bleaching agents (chlorite bleach and bleaching bath additives).
(b) In mixtures with crosslinking agents and finishing agents (for example starch or synthetic finishing agents) and also in combination with very diverse textile finishing processes, especially synthetic resin finishes (for example crease resistant finishes such as "wash-and-wear", "permanent press" and "no-iron"), and also flame resistant finishes, soft handle finishes, anti-soiling finshes or anti-static finishes or antimicrobial finishes.
(c) As additives to various soaps and washing agents.
(d) In combination with other substances having an optical brightening action.

If the brightening process is combined with textile treatment or finishing methods, the combined treatment can in many cases advantageously be effected with the aid of corresponding stable formulations which contain the compounds having an optical brightening action in a concentration such that the desired brightening effect is obtained.

In certain cases, the full effect of the brightener is achieved by an after-treatment. This can be, for example, a chemical treatment (for example acid treatment), a thermal treatment (for example heat) or a combined chemical/heat treatment.

The amount of the optical brighteners to be used according to the invention, relative to the material to be optically brightened, can vary within wide limits. A distinct and durable effect can already be achieved with vary small amounts and in certain cases, for example, with amounts of 0.03% by weight. However amounts of up to about 0.5% by weight can also be used. For most cases of interest in practice, amounts of between 0.05 and 0.5% by weight relative to the material to be brightened, are preferably of interest.

In a fourth aspect of the invention, the optical brighteners are also especially suitable as additives for washing baths or to industrial and household washing agents and they can be added in various ways. They are appropriately added to washing baths in the form of their solutions in water or organic solvents or also in a state of fine division as aqueous dispersions or slurries. They, or their components, are advantageously added to household or industrial washing agents at any phase of the manufacturing process of the washing agent, for example to the so-called "slurry" prior to spray-drying of the washing powder or

during the preparation of liquid washing agent combinations. The compounds can be added both in the form of a solution or dispersion in water or other solvents and also without auxiliaries in the form of a dry brightener powder. However, they can also be sprayed, in the dissolved or pre-dispersed form, onto the finished washing agent.

Washing agents which can be used are the known mixtures of detergent substances, such as, for example, soap in the form of chips and powders, synthetic products, soluble salts of sulphonic acid half-esters of higher fatty alcohols, arylsulphonic acids, which are substituted by higher alkyl and /or polysubstituted by alkyl, carboxylic acid esters with alcohols of medium to higher molecular weight, fatty acid acylaminoalkyl- or aminoaryl-glycerol-sulphonates, phosphoric acid esters of fatty alcohols and the like. So-called "builders" which can be used are, for example, alkali metal polyphosphates and alkali metal polymeta-phosphates, alkali metal pyrophosphates, alkali metal salts of carboxyethylcellulose and other "soil redeposition inhibitors", and also alkali metal silicates, alkali metal carbonates, alkali metal borates, alkali metal perborates, nitrilotriacetic acid, ethylenediamine-tetraacetic acid and foam stabilisers, such as alkanolamides of higher fatty acids. Furthermore, the washing agents can contain, for example: antistatic agents, superfatting skin protection agents, such as lanolin, enzymes, antimicrobial agents, perfumes and dyestuffs.

The brighteners have the particular advantage that they are also effective in the presence of active chlorine donors, such as, for example, hypochlorite and can be used without substantial loss of the effects in washing baths with non-ionic washing agents, for example alkylphenol polyglycol ethers. Also in the presence of perborate or peracids and activators, for example tetraacetylglycoluril or ethylenediamine-tetraacetic acid are the new brighteners very stable both in pulverulent washing agent and in washing baths.

The brighteners according to the invention are added in amounts of 0.005 to 2% or more and preferably of 0.03 to 0.5%, relative to the weight of the liquid or pulverulent ready-to-use washing agent. When they are used to wash textiles made of cellulose fibres, polyamide fibres, cellulose fibres with a high grade finish, wool and the like, wash liquors which contain the indicated amounts of the optical brighteners according to the invention impart a brilliant appearance in daylight.

The washing treatment is carried out, for example, as follows:

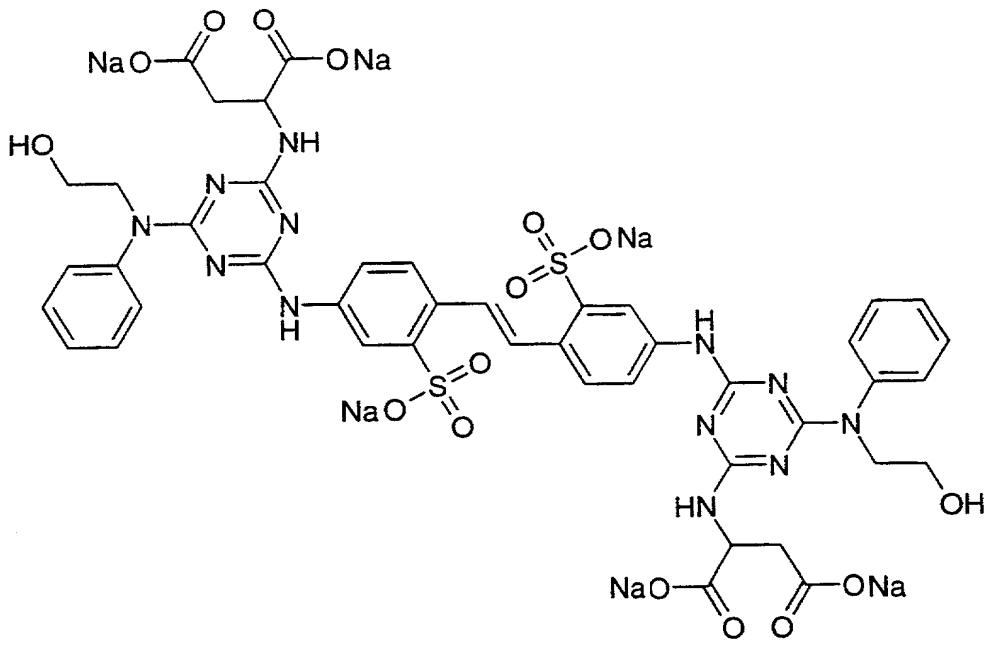
The indicated textiles are treated for 1 to 30 minutes at 5° to 100°C and preferably at 25° to 100°C in a wash bath which contains 1 to 10 g/kg of a composite washing agent containing builders and 0.05 to 1% relative to the weight of the washing agent, of the brighteners claimed. The liquor ratio can be 1:3 to 1:50. After washing, the textiles are rinsed and dried in the customary manner. The wash bath can contain, as a bleach additive, 0.2 g/l of active chlorine (for example in the form of hypochlorite) or 0.1 to 2 g/l of sodium perborate.

The brighteners according to the invention can also be applied from a rinsing bath with a "carrier". For this purpose the brightener is incorporated in a soft rinsing agent or in another rinsing agent, which contains, as the "carrier", for example, polyvinyl alcohol, starch, copolymers on an acrylic basis or formaldehyde/urea or ethylene-urea or propylene-urea derivatives, in amounts of 0.005 to 5% or more and preferably of 0.2 to 2%, relative to the rinsing agent. When used in amounts of 1 to 100 ml, and preferably of 2 to 25 ml, per litre of rinsing bath, rinsing agents of this type, which contain the brighteners according to the invention, impart brilliant brightening effects to very diverse types of treated textiles.

In a fifth aspect of the invention, the compounds of formula (1) are also suitable for removing stain in a photographic material which comprises a silver halide photographic light-sensitive material and, more detailedly, to a process thereof, wherein the improvement is made on the prevention of a colour stain and particularly the prevention of a colour dye stain caused in the course of processing said silver halide photographic light-sensitive material by a colour developer and a bleach-fix bath.

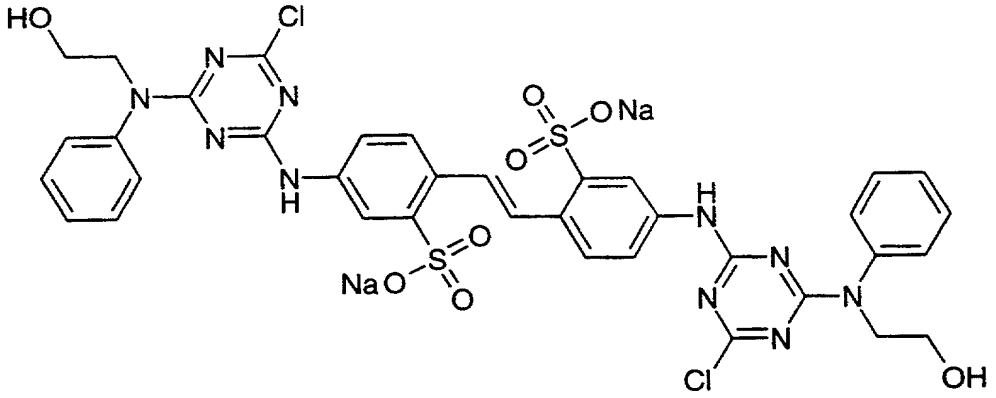
The following Examples serve to illustrate the invention; parts and percentages are by weight, unless otherwise stated.

Example 1



(2)

18.4g. of cyanuric chloride are dissolved in 100ml. of acetone and the solution added to 100g. of ice contained in a reaction vessel. A solution of 18.4g. of 4,4'-diamino-2,2'-stilbene disulphonic acid sodium salt in 330ml. of water is then added over 10 minutes at 5°C. 50ml. of a 1 molar aqueous solution of sodium carbonate are then added over 10 minutes. 14.55g. of N-2-hydroxyethyl aniline are then added, the temperature raised to 35°C, whereby the pH is maintained between 7 and 7.5, and the mixture stirred for a further 2 hours. The precipitated product is filtered, washed with water and dried to yield 39g of a compound of formula:



(2a)

Analysis for $C_{36}H_{30}Cl_2N_{10}Na_2O_8S_2$:

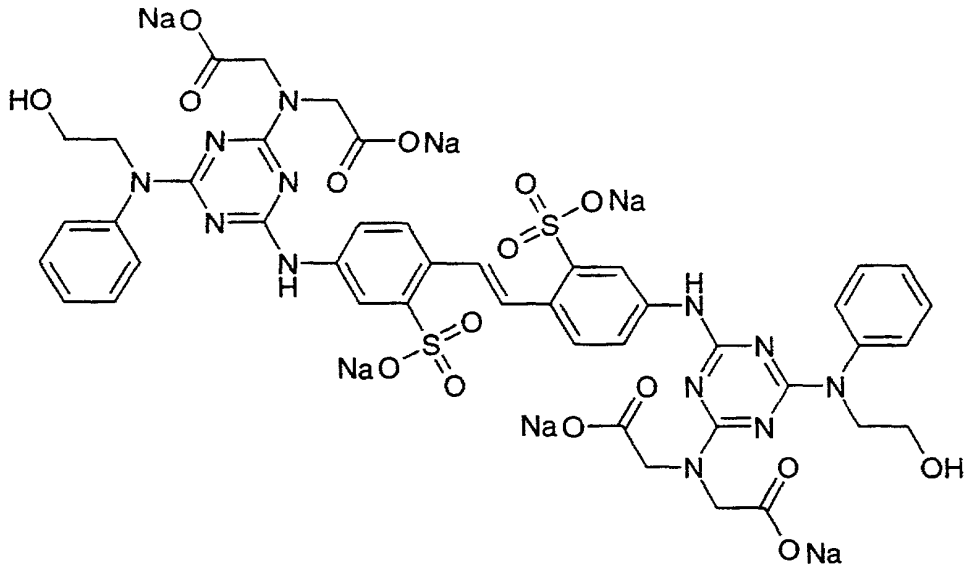
calculated: C 47.32%, H 3.54%, Cl 7.76%, N 15.33%, S 7.02%;
found: C 47.1%, H 4.0%, Cl 7.7%, N 15.5%, S 6.7%.

To 10g. of the compound of formula (2a) in 150ml. of water, 3.4g. of aspartic acid are added and the mixture heated to 70°C, the pH being maintained at between 8 and 8.5 by the addition of a 32% aqueous sodium hydroxide solution. After 2 hours at this temperature, the reaction is completed. The pH of the mixture is then adjusted to 3 by the addition of 37% aqueous hydrochloric acid, the temperature being maintained at 70°C. The precipitated free acid is filtered, suspended in a methanol/water mixture and the pH adjusted to 9 by the addition of a 32% aqueous sodium hydroxide solution. The precipitated product is filtered and dried to yield 8.8g. of the compound of formula (2).

Analysis for $C_{44}H_{38}N_{12}Na_6O_{16}S_2.10.5H_2O$:

calculated: C 38.23%, H 4.31%, N 12.17%, Na 9.99%, S 4.64%;
found: C 38.2%, H 4.5%, N 12.2%, Na 9.8%, S 4.6%.

Example 2



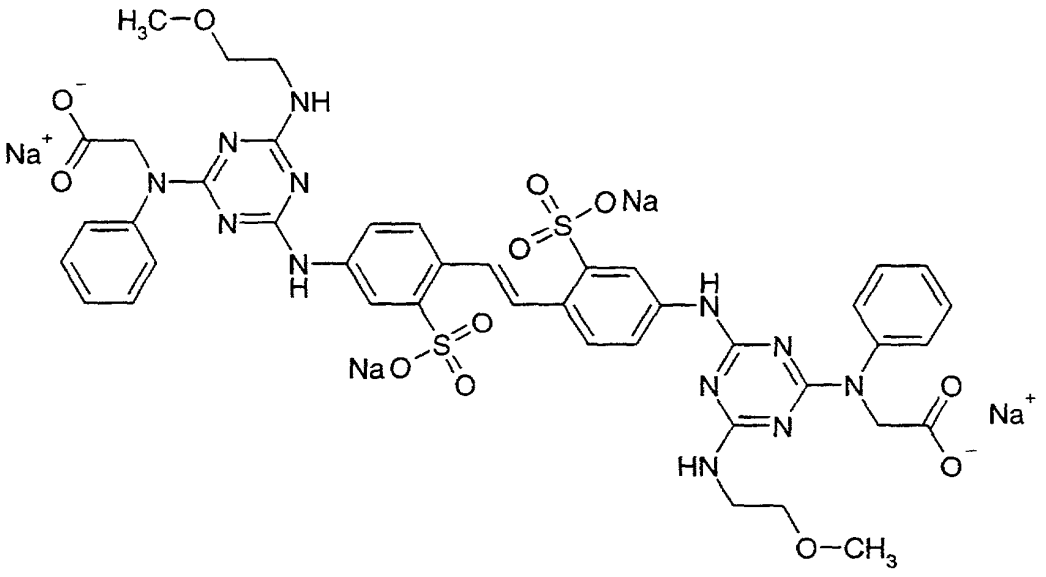
(3).

To 40g. of ice/water, 12.5g. of cyanuric chloride are added, followed by 0.5g. of polyethylene glycol and the mixture stirred for 15 minutes. A solution of 12g. of 4,4'-diamino-2,2'-stilbene disulphonic acid sodium salt in 90ml. of water is then added over 10 minutes at 5°C. 20g. of a 17% aqueous solution of sodium carbonate in 60ml. of water are then added and the mixture stirred at 5°C until the pH falls to 5.5. The contents of the flask are then concentrated under vacuum to a weight of 193g., whereby a 20% solution of compound (2a) results which, according to HPLC, is identical to that obtained in Example (1) above.

This solution is then treated in a manner identical to that described above for the preparation of compound (2), except that the aspartic acid is replaced by the equivalent amount of iminodiacetic acid. The compound of formula (3) obtained exhibits the following elemental analysis for $C_{44}H_{38}N_{12}Na_6O_{16}S_2.16H_2O$:

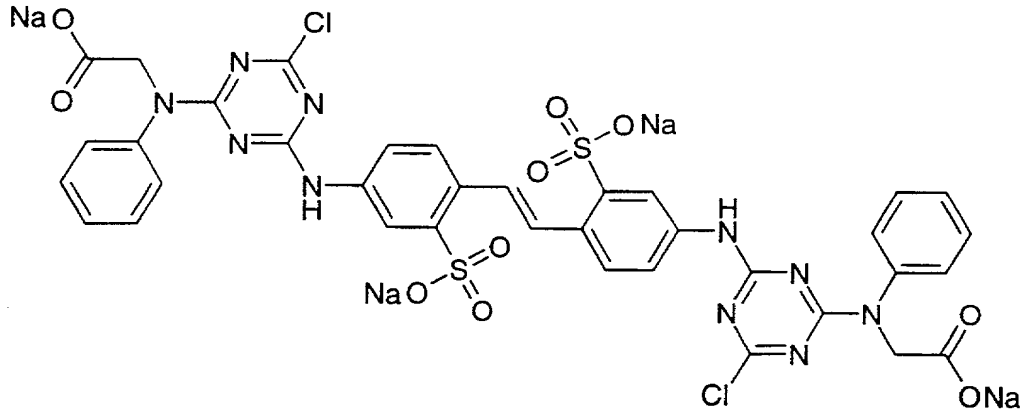
calculated: C 35.68%, H 4.75%, N 11.35%, S 4.33%;
found: C 35.52%, H 4.59%, N 11.27%, S 4.43%.

Example 3



(4).

16g of cyanuric chloride are dissolved in 90ml of acetone and the solution poured onto 90g of ice/water. A solution of 20g of 80.8% 4,4'-diamino-2,2'-stilbene disulphonic acid in 200ml of water and 90g of ice/water is then added to the cyanuric chloride suspension over 20 minutes. The pH is adjusted to 4.5-5.0 by the addition of 43.5ml of an aqueous 1M sodium carbonate solution, the temperature being maintained below 5°C. After stirring for 30 minutes, 13.6g. of 97% N-phenylglycine and 43.5ml of an aqueous 1M sodium carbonate solution are added. The mixture is then stirred for 3 hours during which time the temperature rises to 20oC, the pH being maintained at 6.8-7.5 by the addition of 10.9g of 32% aqueous sodium hydroxide solution. The reaction mixture is filtered, the filtrate concentrated, diluted with 200ml of methanol and the solution poured into 1l of isopropanol. The precipitated product is separated by filtration and dried under vacuum at 80°C yielding the compound of formula



(3a)

The product obtained exhibits the following elemental analysis for $C_{36}H_{24}Cl_2N_{10}Na_4O_{10}S_2.7H_2O.0.2NaCl$:

calculated: C 38.50%, H 3.45%, Cl 6.95%, N 12.50%, S 5.71%;
found: C 38.46%, H 3.60%, Cl 7.01%, N 12.59%, S 5.67%.

5.5g of the compound (3a) are stirred in 20ml of water and 1g of 98% 2-methoxy-ethylamine is added. The mixture is heated to 85°C while maintaining the pH at 8.5-9.0 by the addition of 1.1g of 32% aqueous sodium hydroxide solution. After 2 hours the mixture is cooled, the pH adjusted to 3.0 by the addition of 2N hydrochloric acid and 50ml of acetone added. The suspension is filtered, the solid added to 50ml of methanol and a 32% methanolic solution of sodium methylate added to pH 9.3. The alcohol is then evaporated and the final product dried under vacuum at 80°C to yield compound (4).

The product obtained exhibits the following elemental analysis for $C_{42}H_{38}N_{12}Na_4O_{12}S_2.7.8H_2O.0.4NaCl$:

calculated: C 41.20%, H 4.60%, Cl 1.10%, N 13.70%, S 5.23%;
found: C 41.25%, H 4.47%, Cl 1.07%, N 13.78%, S 5.20%.

Example 4

Bleached cotton swatches are treated by the exhaust method in an aqueous bath having the following composition:

0.2% of Compound (4) as 100% active substance, based on the weight of the fibre,
0.5ml/l Ultravon® UV,
20ml/l 3% aqueous sodium hydroxide solution,
2ml/l 10% aqueous water glass solution and
3ml/l 35% aqueous hydrogen peroxide solution.

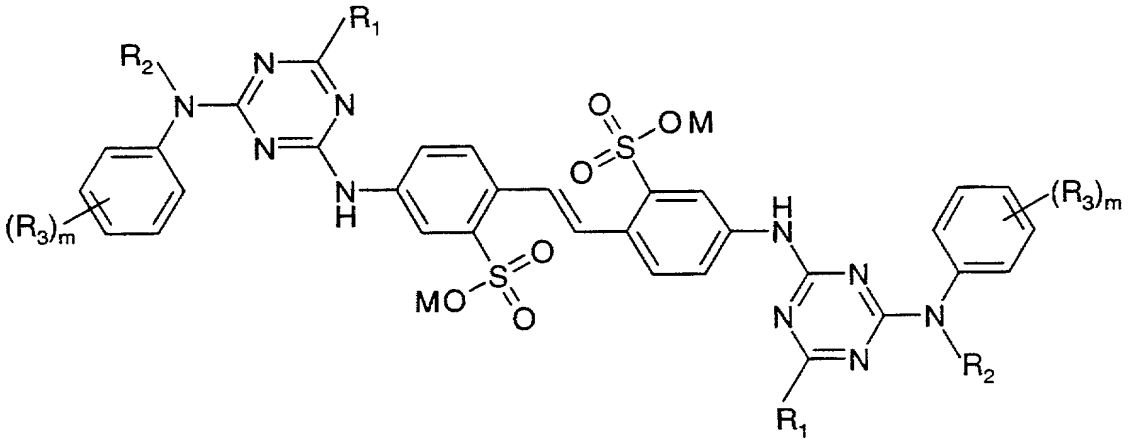
The treatment is conducted at a liquor ratio of 1:40 for 30 minutes at from 25 to 95 °C, then for a further 30 minutes at 95°C and, finally cooled to 30°C. The swatches are removed from the treatment bath, rinsed and dried in an oven at 60°C.

The whiteness of the swatches is measured according to the method of Ganz, which is described in detail in The Ciba-Geigy Review, 1973/1 and also in the article "Whiteness Measurement", ISCC Conference on Fluorescence and the Colorimetry of Fluorescent Materials, Williamsberg, February 1972, published in the Journal of Color and Appearance, 1, No. 5 (1972).

The whiteness value measured for the swatches treated as described is 127.

Claims

1. A compound having the formula:



(1)

wherein each

R_1 represents, independently, a linear C_1-C_4-alkylene residue which is unsubstituted or substituted by hydroxy, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-hydroxy- or alkoxy-alkoxy, -OCOM, -OCOC_1-C_4-alkyl, or an amino acid residue from which a hydrogen atom on the amino group has been removed; each

R_2 represents, independently, a linear C_1-C_4-alkylene residue which is unsubstituted or substituted by hydroxy, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-hydroxy- or alkoxy-alkoxy, -OCOM, -OCOC_1-C_4-alkyl, -CO_2M, CO_2C_1-C_4-alkyl SO_3M or phenoxy which is unsubstituted or substituted by halogen, C_1-C_4-alkyl or C_1 -C_4-alkoxy, -CO_2M or -CO_2C_1-C_4-alkyl, NH_2 or mono- or disubstituted amino; or phenyl which is unsubstituted or substituted by 1 to 3 SO_3M, SO_2NHC_1-C_4- alkyl,-SO_2NH_2, -CO_2M, -CO_2C_1-C_4-alkyl, -$CONH_2$, -CONHC_1-C_4-alkyl, -NHCOC_1-C_4-alkyl or mono- or disubstituted amino groups; each

R_3 represents, independently, hydrogen, C_1-C_4-alkyl, halogen, cyano, SO_3M, -SO_2NH_2, SO_2NHC_1-C_4-alkyl, -CO_2M, -CO_2C_1-C_4-alkyl, -$CONH_2$, -CONHC_1-C_4-alkyl, or -NHCOC_1-C_4-alkyl;

M is hydrogen, an alkali metal atom, ammonium or a cation formed from an amine and

m is an integer of 1 to 3.

2. A compound according to claim 1 in which both of the R_1 groups, the R_2 groups and the R_3 groups are identical.

3. A compound according to claim 2 in which each R_1 is an amino acid residue and each has the formula -NH-CH(CO_2H)-R_4 in which R_4 is hydrogen or a group having the formula -CHR_5R_6 in which R_5 and R_6, independently, are hydrogen or C_1-C_4-alkyl optionally substituted by one or two substituents selected from hydroxy, thio, methylthio, amino, carboxy, sulfo, phenyl, 4-hydroxyphenyl, 3,5-diiodo-4-hydroxyphenyl, β-indolyl, β-imidazolyl and NH=C(NH_2)NH-.

4. A compound according to claim 3 in which the amino acid from which the amino acid residues R_1 are derived is glycine, alanine, sarcosine, serine, cysteine, phenylalanine, tyrosine (4-hydroxyphenylalanine), diiodotyrosine, tryptophan (β-indolylalanine), histidine ((β-imidazolylalanine), α-aminobutyric acid, methionine, valine (α-aminoisovaleric acid), norvaline, leucine (α-aminoisocaproic acid), isoleucine (α-amino-β-methylvaleric acid), norleucine (α-amino-n-caproic acid), arginine, ornithine (α,δ-diaminovaleric acid), lysine (α,ε-diaminocaproic acid), aspartic acid (aminosuccinic acid), glutamic acid (α-aminoglutaric acid), threonine, hydroxyglutamic acid or taurine, or a mixture or an optical isomer thereof.

5. A compound according to claim 4 in which the amino acid from which the amino acid residues R_1 are derived is sarcosine, taurine, glutamic acid or aspartic acid.

6. A compound according to any of claims 1 to 5 in which the amino acid from which each amino acid residue R_1 is derived is aspartic acid or iminodiacetic acid.

7. A compound according to claims 1 or 2 in which R_1 is a linear C_1-C_4-alkylene residue which is unsubstituted or substituted by hydroxy, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-hydroxy- or alkoxy-alkoxy, -OCOM, -OCOC_1-C_4-alkyl, M being as previously defined.

8. A compound according to claim 7 in which R_1 is a linear C_1-C_4-alkylene residue which is unsubstituted or substituted by hydroxy, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-hydroxy- or alkoxy-alkoxy.

9. A compound according to claim 8 in which R_1 is a linear C_1-C_4-alkylene residue

which is substituted by hydroxy or C_1-C_4-alkoxy.

10. A compound according to any one of claims 1 to 9 in which the group R_2 represents a linear C_1-C_4-alkylene residue which is unsubstituted or substituted by hydroxy, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-hydroxy or alkoxyalkoxy, -OCOM, -OCOC$_1$-C_4-alkyl, -CO_2M, -CO_2C_1-C_4-alkyl, SO_3M, phenoxy which is unsubstituted or substituted by halogen, C_1-C_4-alkyl, C_1 -C_4-alkoxy, -CO_2M or -CO_2C_1-C_4-alkyl, NH_2 or mono- or disubstituted amino.

11. A compound according to claim 10 in which the group R_2 represents a methylene, ethylene or propylene residue which is substituted by hydroxy, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-hydroxy- or alkoxy-alkoxy, -OCOM, -OCOC$_1$-C_4-alkyl, -CO_2M, -CO_2C_1-C_4-alkyl, SO_3M or di-C_1-C_4-alkylamino, whereby M is as defined in claim 1.

12. A compound according to claims 10 or 11 in which R_2 is hydoxyethyl, hydroxypropyl, ethoxyethyl, hydroxyethoxyethyl, methoxyethoxyethyl, an acetic or propionic acid residue or methyl or ethyl esters thereof, an ethyl or methyl acetate, dimethylaminoethyl or ethyl sulphonic acid or the sodium salt thereof.

13. A compound according to claim 12 in which R_2 is hydoxyethyl or a sodium acetate residue.

14. A compound according to claims 1 or 2 in which each R_2 is phenyl which is unsubstituted or substituted by 1 to 3 SO_3M, SO_2NHC_1-C_4- alkyl,-SO_2NH_2, -CO_2M, -CO_2C_1-C_4-alkyl, -$CONH_2$, -CONHC$_1$-C_4-alkyl, -NHCOC$_1$-C_4-alkyl or mono- or disubstituted amino groups, wherein M is as defined in claim 1,

15. A compound according to claims 14 in which each R_2 is phenyl which is unsubstituted or substituted by one SO_3M,-SO_2NH_2 or -NHCOC$_1$-C_4-alkyl group.

16. A compound according to claims 14 or 15 in which each R_2 is phenyl.

17 A compound according to any one of the preceding claims in which R_3 represents hydrogen, C_1-C_4-alkyl, halogen, cyano, SO_3M, -SO_2NH_2, SO_2NHC_1-C_4-alkyl, -CO_2M, -

CO_2C_1-C_4-alkyl, -$CONH_2$, -$CONHC_1$-C_4-alkyl, or -$NHCOC_1$-C_4-alkyl, M being defined as in claim 1 and m is 1.

18. A compound according to claim 17 in which R_3 represents hydrogen.

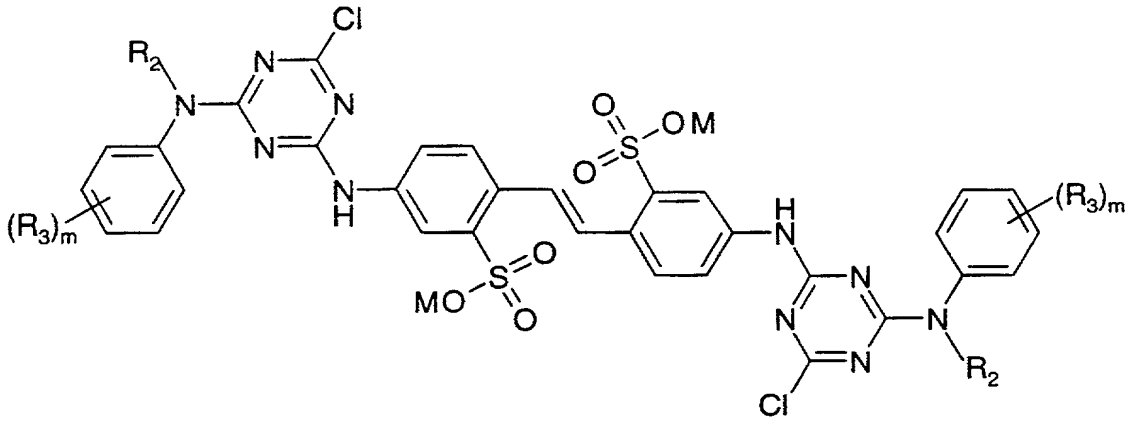
19. A compound according to any of the preceding claims in which M is hydrogen, Na, K, Ca, Mg, ammonium, mono-, di-, tri- or tetra-C_1-C_4alkylammonium, mono-, di- or tri-C_1-C_4-hydroxyalkylammonium or ammonium that is di- or tri-substituted with a mixture of C_1-C_4-alkyl and C_1-C_4-hydroxyalkyl groups.

20. A compound according to claim 19 in which each M is hydrogen or Na.

21. A compound of formula 1 in which:
R_1 is an amino acid residue derived from aspartic acid or iminodiacetic acid,
R_2 is hydroxyethyl,
R_3 is hydrogen and
M is sodium.

22. A compound of formula 1 in which:
R_1 is a 2-methoxyethylamino residue,
R_2 is a sodium acetate residue,
R_3 is hydrogen and
M is sodium.

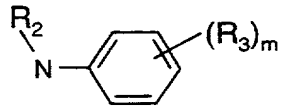
23. A compound of the formula:



(5)

in which R_2, R_3, M and m are as defined in claim 1.

24. Use of the compound of formula (5) of claim 23 for the preparation of a compound of the formula (1).

25. A process for the preparation of a compound of formula (1) by reacting, under known reaction conditions, cyanuric chloride, successively, in any desired sequence, with each of 4,4'-diamino-2,2'-stilbene disulphonic acid, an amino compound capable of introducing a group  in which R_2, R_3 and m have their previous significance, and

a compound capable of introducing a group R_1, in which R_1 has its previous significance.

26. Use of the compounds of formula (1) as optical brightening agents for synthetic or natural organic materials.

27. Use of the compounds of formula (1) according to claim 26 as optical brightening agents for paper in pulp, size-press or coating applications.

28. Use of the compounds of formula (1) according to claim 26 as optical brightening agents for textile materials, especially cotton and polyamide materials as well as mixtures of the same and other synthetic fibres.

29. Use of the compounds of formula (1) according to claim 26 as optical brightening agents in detergent compositions.

30. Use of the compound of formula (1) for removing stain in photographic materials.

31. A composition for whitening synthetic or natural organic materials or for removing stain from photographic materials, which contains water, a fluorescent whitening agent according to claim 1 and, optionally, auxiliaries.

32. Brightener compositions according to claim 31 containing water and, in each case based on the weight of the formulation, from 3 to 25% by weight, preferably from 5 to 15% by weight of the above defined fluorescent whitening agent mixture and also 0 to 60%, preferably 5 to 50% by weight, of auxiliaries.

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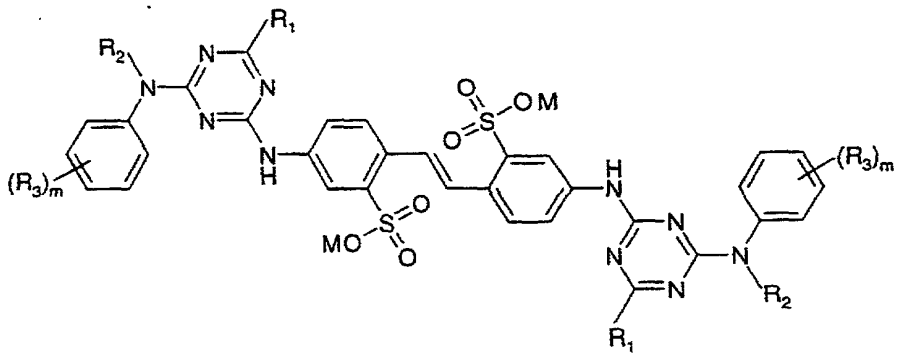
(54) Title: TRIAZINYLAMINOSTILBENE DERIVATIVE AS FLUORESCENT WHITENING AGENTS



(1)

(57) Abstract: The present invention relates to compounds having formula (1): wherein each R_1 represents, independently, a linear C_1-C_4-alkylene residue which is unsubstituted or substituted by hydroxy, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-hydroxy- or alkoxy-alkoxy, -OCOM, -OCOC$_1$-C_4-alkyl, or an amino acid residue from which a hydrogen atom on the amino group has been removed; each R_2 represents, independently, a linear C_1-C_4-alkylene residue which is unsubstituted or substituted by hydroxy, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-hydroxy- or alkoxy-alkoxy, -OCOM, -OCOC$_1$-C_4-alkyl, -CO_2M, CO_2C_1-C_4-alkyl SO_3M or phenoxy which is unsubstituted or substituted by halogen, C_1-C_4-alkyl or C_1-C_4-alkoxy, -CO_2M or CO_2C_1-C_4-alkyl, NH_2 or mono- or disubstituted amino; or phenyl which is unsubstituted or substituted by 1 to 3 SO_3M, SO_2NHC_1-C_4-alkyl, -SO_2NH_2, -CO_2M, -CO_2C_1-C_4-alkyl, -$CONH_2$, -CONHC$_1$-C_4-alkyl, -NHCOC$_1$-C_4-alkyl or mono- or disubstituted amino groups; each R_3 represents independently, hydrogen, C_1-C_4-alkyl, halogen, cyano, SO_3M, -SO_2NH_2, SO_2NHC_1-C_4-alkyl, -CO_2M, -CO_2C_1-C_4-alkyl, -$CONH_2$, -CONHC$_1$-C_4-alkyl, or -NHCOC$_1$-C_4-alkyl; M is hydrogen, an alkali metal atom, ammonium or a cation formed from an amine and m is an integer of 1 to 3, a process for their preparation and use of the compounds as optical brightening agents for synthetic or natural organic materials or for removing stain in photographic materials.

WO 01/19804 A1

US Case **PW/3-22076/US/A**

DECLARATION AND POWER OF ATTORNEY FOR U.S. PATENT APPLICATIONS

☐ Original ☐ Supplemental ☐ Substitute ☒ PCT

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if more than one name is listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Trazinylaminostilbene derivative as fluorescent whitening agents

which is described and claimed in:

☐ the attached specification.

☐ the specification in U.S. Application No. filed _____ (day/month/year), and as amended on _____ (day/month/year) (if applicable).

☒ the specification in International Application No. **PCT/EP 00/08621** filed **04/09/00** (day/month/year)

assigned U.S. Application No. (if applicable), and as amended

- ☐ under PCT Article 19 on _____ (day/month/year) (if applicable)
- ☐ under PCT Article 34 on _____ (day/month/year) (if applicable)
- ☐ and further amended on _____ (day/month/year) (if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose all information which is known by me to be material to the patentability of this application as defined in 37 C.F.R. § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. § 119 (a)-(d) of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America relating to this subject matter having a filing date before that of the application on which priority is claimed:

COUNTRY/REGION (OR PCT)	APPLICATION No.	FILING DATE (day/month/year)	PRIORITY CLAIMED	
Europe (designating DE)	**99810813.8**	**10/09/1999**	☒ Yes	☐ No
			☐ Yes	☐ No
			☐ Yes	☐ No
			☐ Yes	☐ No
			☐ Yes	☐ No

I hereby claim the benefit under 35 U.S.C. § 119 (e) of any United States provisional application(s) listed below:

APPLICATION NO.	FILING DATE (day/month/year)

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s) or PCT international application(s) designating the United States listed below and, insofar as the application discloses and claims subject matter in addition to that disclosed in the prior copending application, I acknowledge the duty to disclose all information known by me to be material to patentability as defined in 37 C.F.R. § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

U.S. APPLICATION No.	FILING DATE (day/month/year)	STATUS		
		☐ Patented	☐ Pending	☐ Abandoned
		☐ Patented	☐ Pending	☐ Abandoned
		☐ Patented	☐ Pending	☐ Abandoned
		☐ Patented	☐ Pending	☐ Abandoned
		☐ Patented	☐ Pending	☐ Abandoned

PCT APPLICATION No. (designating the U.S.)	INTERNATIONAL FILING DATE (day/month/year)	U.S. APPLICATION No. (if any)	STATUS
			☐ Patented
			☐ Pending
			☐ Abandoned

I hereby appoint the following attorneys and agents, associated with Customer No. 000324, each of them with full power of substitution, revocation and appointment of associates, to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. § 1001, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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